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The Response of Phosphonium Ionic Liquids in Lubricating Greases with Respect to various Tribological contacts

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Introduction

As we move towards a more sustainable world, the electrification of everyday transport vehicles is a major change driver. Electric vehicles (EV) offer the promise of reduced carbon emissions from transportation and a reduced impact on the environment. In order to achieve their maximum potential EVs must identify and improve multiple aspects in their design, lubrication being a significant one. Furthermore - improved lubrication reduces the amount of wear on equipment, extending usable life of the component.

There are many challenges and opportunities confronting today's electric vehicle (EV) manufacturers. This includes, but is not limited to new lubricants for drivetrains, cooing requirements (thermal management), dielectric properties, gear and bearing changes (new engine layouts), higher RPMs, and copper compatibility. When selecting EV lubricants and greases, companies often rely on iterative improvements to formulations designed for internal combustion engines. These lubrication systems present challenges and fail to substantially improve system efficiency. The requirements for EV lubrication are significantly different than ICE engines. Running with conventional or modified lubricants in EV lose as much as 30% of efficiency due to losses directly related to lubrication.[1,2,3] This presentation demonstrates the responses of phosphonium ionic liquids as metal-free/ashless additives to deliver AW/EP (antiwear/extreme pressure) properties and thermal/electrical conductivity improvements, beneficial to this application with specific focus on lubricating greases.

For greases in particular, the additives must enhance the desirable properties, suppress undesirable ones, and add new properties that improve the system as a whole.[4] Further to this, greases need to be designed as "fill for life" in many systems. Any resulting formulation must demonstrate the potential to be long lasting and maintain its efficacy over a defined time period of the part (or vehicle). A further complicating factor specific the bearings are the type of EV or hybrid system - from fully electric to hybrid systems there are different and specific needs. EV motors can spin as high as 20,000 (rpm) which can also lead to issues of added noise and areas of high heat. The solutions used must be consistent, have the right viscosity, provide oxidation resistance, and shear stability in addition to the requirements previously mentioned.

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4. Aniderman, D. (2017). The chemistry and function of lubricant additives. Tribol. Lubric. Technol. 73, 18–29.

With higher demands on automotive electric systems, the risk of motor charge build-ups and relative consequences resulted in an increased focus on conductive properties of fluids and electrically conductive greases. Passage of electric currents through lubricating contacts and micro pitting are the known cause for bearings damage and have been studied for years to minimize bearing damage. Therefore, lubrication under charged conditions is gaining momentum, hence, more studies needed to be conducted in order to understand how the main grease components will be affected by electrical field.[5]

The focus of this study has been on the responses of a more sustainable additive system in lithium complex greases. Reason for the selection of this thickener system was since this type of grease is commonly used for bearings in automotive and industrial application.

During the decades, more advanced additive systems have been developed in order to maximize the efficiency of vehicles by e.g., reducing the friction between the moving parts. Phosphorus products have a long- and well-established history of use as additives in lubrication due to their beneficial properties improving AW and EP. These include phosphate esters, phosphites and phosphate amines[6,7,8] among others. Secondary benefits include improvement in fuel economy and increased power.

In 2012, the first reports of oil miscible phosphonium ionic liquids appeared and added a new class of phosphorus compounds to the lubrication field[9] Wear protection occurs by tribofilm formation on the metal surfaces. These focused primarily on systems with traditional base oils for internal combustion engines.[10,11,12,13,14,15] These beneficial properties can be observed with as low as 0.5-1.0 wt% loading levels.

Several phosphonium ionic liquids have been identified as viable candidates for both base oil and grease formulations.[16,17,18,19] However, as applications continue to develop and evolve, particularly in electric vehicles - further improvements and research is required.

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Phosphonium salts have previously been reported for a variety of applications and as such have well established synthetic routes and are produced at a variety of scales.[20,21,22] These systems can be tailored by judicial selection of phosphine, followed by alkylation and if required, anion exchange (Figure 1) making them very attractive moieties for development. These molecules have many advantageous properties for lubrication such as high thermal stability, electrical conductivity, wide liquid range, elastomer compatibility, ashless, ionic nature, low volatility and low flammability.

Ionic liquids have been reported as neat solutions for these applications as they provide low coefficient of friction and high wear resistance, however they have caused issues for tribo corrosive effects when bearing current was high, and they may be cost prohibitive in some cases.[23] For the purposes of this study, only phosphonium ionic liquids were investigated as additives rather than neat formulations.

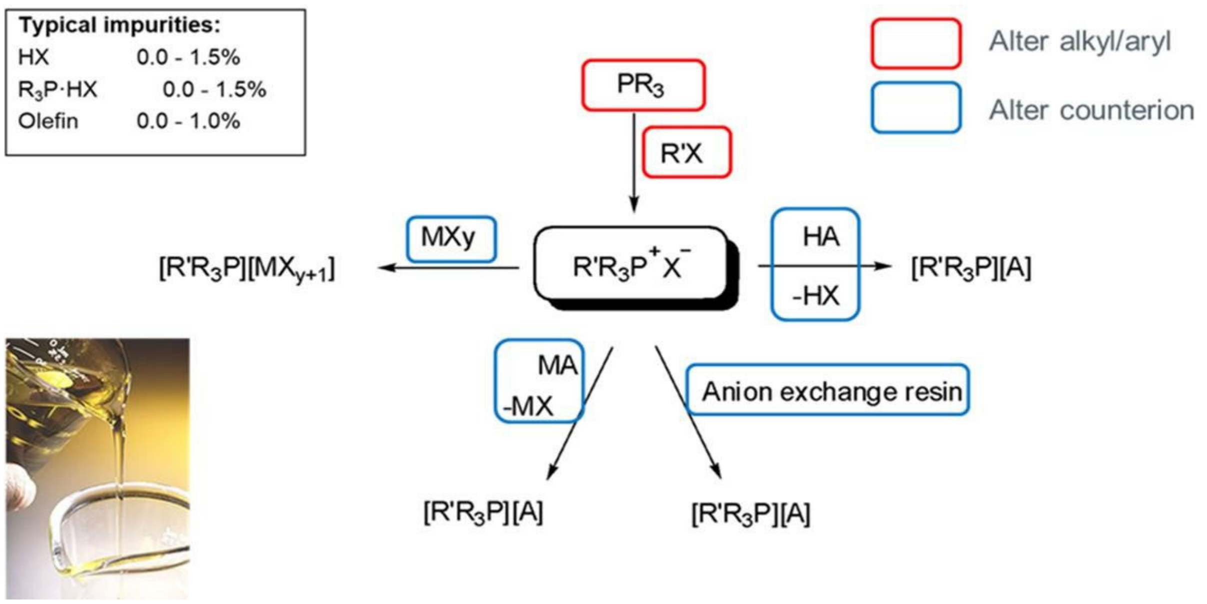

Figure 1: Synthesis of Phosphonium Ionic Liquids

Phosphorus- based ionic liquid additives can withstand harsh conditions of EV systems, facilitating heat transfer and improving operating efficiency. Heat transfer is a critical issue in lubricants for EVs as they must be able to transfer heat from areas with local and high heat intensity. Furthermore, due to the tunability of the alkyl substituents, one can synthesize molecules that are soluble in a variety of different base oils.

Phosphonium ionic liquids and salts have provided good AW/EP properties at relatively low loadings (0.5-1 wt%) of material into a base oil or grease formulation. In this study we aim to further investigate the use of phosphonium ionic liquids in greases with an end goal of applicability in electric and internal combustion applications. Overall, this work is critical to

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improve fuel efficiency and energy usage, as well as help to enable electrification of motor vehicles further.

Experimental Work and Discussion

1. Synthesis of Ionic Liquids

For lubrication applications, oil soluble systems such as [P4444][DEHP] (***3***) and [P8888][DEHP] (***4***) are attractive starting points which can be readily synthesized (Figure 2). The precursor phosphonium salts tetrabutylphosphonium bromide [P4444][Br] (***1***) and tetraoctylphosphonium bromide, [P8888][Br] can be reacted with LiDEHP in stoichiometric quantities to get good conversion to the desired salts (***3***) and (***4***). The details of the synthesis have been previously reported.[24]

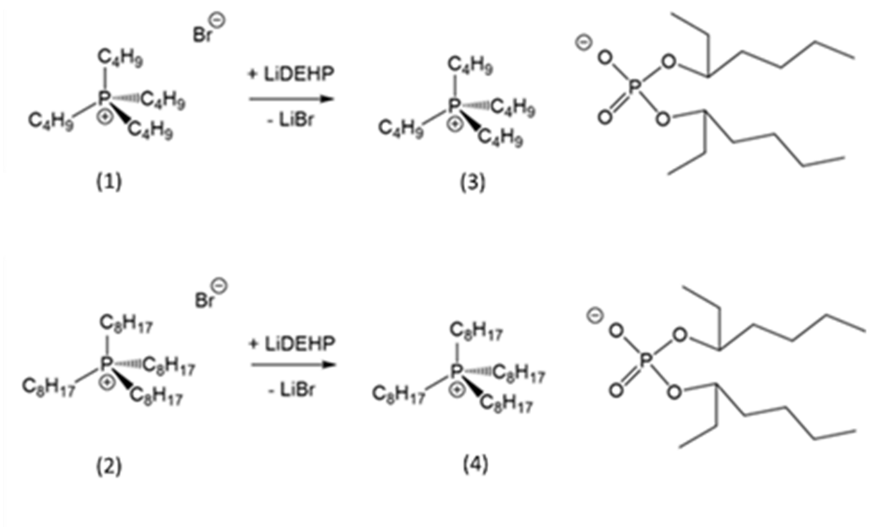

Figure 2: Synthesis of [P4444][DEHP] (***3***) and [P8888][DEHP] (***4***)

2. Thermal stability of Phosphonium Ionic Liquids

Phosphonium salts are typically very resilient to high thermal stresses making them ideal candidates for the high heat stress environment of ICE and EV motors. Thermogravimetric analysis (TGA) of compounds ***3*** (a) and ***4*** (b), are below. in Figure 2. In each case, there is no onset degradation below 200 $^{\circ}$C. The ionic system ***4*** shows a very high thermal stability with no observed degradation up to almost 300 $^{\circ}$C. Based on this observation - this ionic specie is believed to be able to maintain significant heat impact over time making it well suited for the long-life targets of EV lubrication in particular. A common feature of the phosphonium ionic liquids is that when they are heated under inert conditions - the thermal stability is further increased, making the effect magnified when these conditions can be satisfied (Figure 3). With many EV bearings operating a temperature -40 to 160 °C, these molecules are well suited for the thermal constraints of the EV bearing.

24. Bradaric, C.J. et al. Green Chemistry, **2003**, 5, 143-152

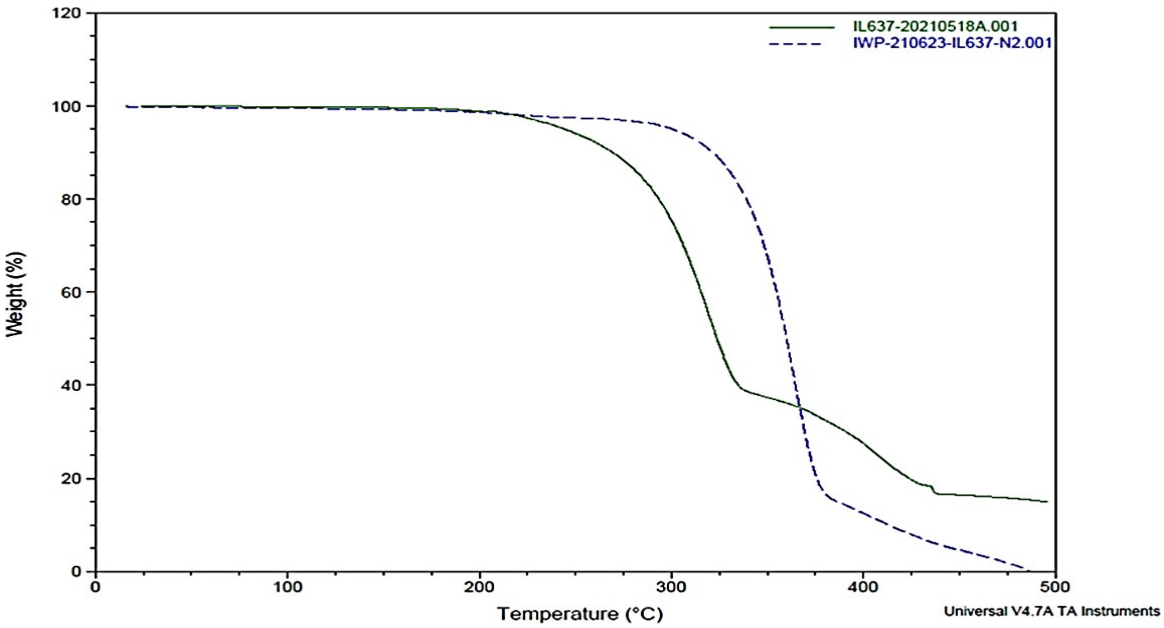

Figure 3: TGA of compound ***3*** under air (green) and nitrogen (blue)

3. Viscosity and Density of Ionic Liquids

Phosphonium ionic liquids have a wide range of viscosities (Table 1). These can impact the given viscosity of a formulation when added in high loadings. Of note, with the phosphonium ionic liquids ***3*** (***IL3***) and ***4*** (***IL4***) with only addition of 5 wt% or less - these do not significantly impact the viscosity of the formulations in this paper.

Table 1. Viscosity and density of relevant phosphonium ionic liquids ***3*** and ***4*** at various temperatures.

Ionic liquid	T (°C)	Dynamic Viscosity (mPa.s)	Kinematic Viscosity (mm^2/s)	Density (g/cm^3)
IL3	20	1556.8	1648.8	0.9442
	25	1077.6	1145.5	0.9407
	40	418.8	450.2	0.9302
IL4	20	2547.3	2802.2	0.9090
	25	1895.6	2092.9	0.9057
	40	870.6	971.6	0.8960

4. The Base Oils

In total, four oils with different viscosities have been used. Out of four one is straight cut naphthenic oil with a viscosity of about 560 mm^2/s (cSt) and three base oil blends, with viscosities of about 200, 100 and 75 mm^2/s (cSt) respectively. The base oil blend with 75 mm^2/s (cSt) is a mixture of highly refined naphthenic oil with an aromatic content less than 1 percent and a polyalphaolefin. Some of the characteristics of these base oils are gathered in Table 2.

Table 2. Measured characteristics of the selected base oils.

Remarks	Method, ASTM	Base Oil A	Base Oil B	Base Oil C	Base Oil D
Base oil type	-	Naphthenics	Naphthenics + Paraf Gr II	Naphthenics + Paraf Gr II	Naphthenics + PAO
Viscosity at 40 °C, mm^2/s	D 445	561.2	195.8	99.7	75.1
Viscosity at 100 °C, mm^2/s	D 445	20.6	14.9	9.0	8.7
Aniline Point, °C	D 611	91.6	109	92.25	111.7
Flash Point, °C	D 93	249	253	194	222
Pour Point, °C	D 97	-9	-30	-33	-33
Sulfur Content, wt. %	D 2622	0.0642	0.171	0.0462	0.0049
Cu Corrosion, rating	D 130	1	1	1	1

The idea behind the use of these oils were to investigate whether the base oil viscosity or/and the degree of the solvency could have any impact on the response of the Ionic liquids or not.

5. The Greases

Four lithium complex grease (Grease A, B, C, D) have been produced in a pilot plant at atmospheric pressure. The acids that have been used were 12-hydroxystearate acid (12-HSA) and azelaic acid. In Table 3 some of the properties of the neat lithium complex greases (LiX) are described.

Table 3 Some characteristics of the neat lithium complex greases

Remarks	Method	Grease A	Grease B	Grease C	Grease D
Base Oil	-	Base Oil A	Base Oil B	Base Oil C	Base Oil D
NLGI grade	ASTM D217	2	2	2	2
Thickener content, wt%	-	8.55	11.89	11.97	15.80
Dropping point, °C	IP396	>280	>280	>280	>280
Oil separation, wt%	IP121	3.15	4.62	5.82	4.63
Copper Corrosion, rating	ASTM D4048	1a	1a	1a	1b
Flow Pressure @-20 °C, mbar	DIN 51805	720	295	345	220

Table 3 suggests that Grease A, which is based on a high viscous naphthenic oil with high degree of solvency (the lower the aniline point the higher is the solvency), results to the lowest thickener content, while Grease D with the lowest oil viscosity and the lowest degree of solvency (highest aniline point) requires almost twice amount thickener targeting same consistency (NLGI grade 2). Furthermore, the moderate flowability of Grease A at -20 °C, is a result of the viscosity of the oil (Base Oil A) and its pour point.

6. The Impact of the Additives (ILs) on the Greases

Incorporation of the Ionic Liquids into the greases were conducted in two steps

Step 1: hand mixing with spatula for one minute

Step 2: Four time run through the three-steel-roller mill with minimum gap size.

6.1. Rheological Study

Rheological study has been conducted by applying the rotational program (shear stress vs shear rate) at constant temperature (25 °C) with cone on plate as the selected geometry

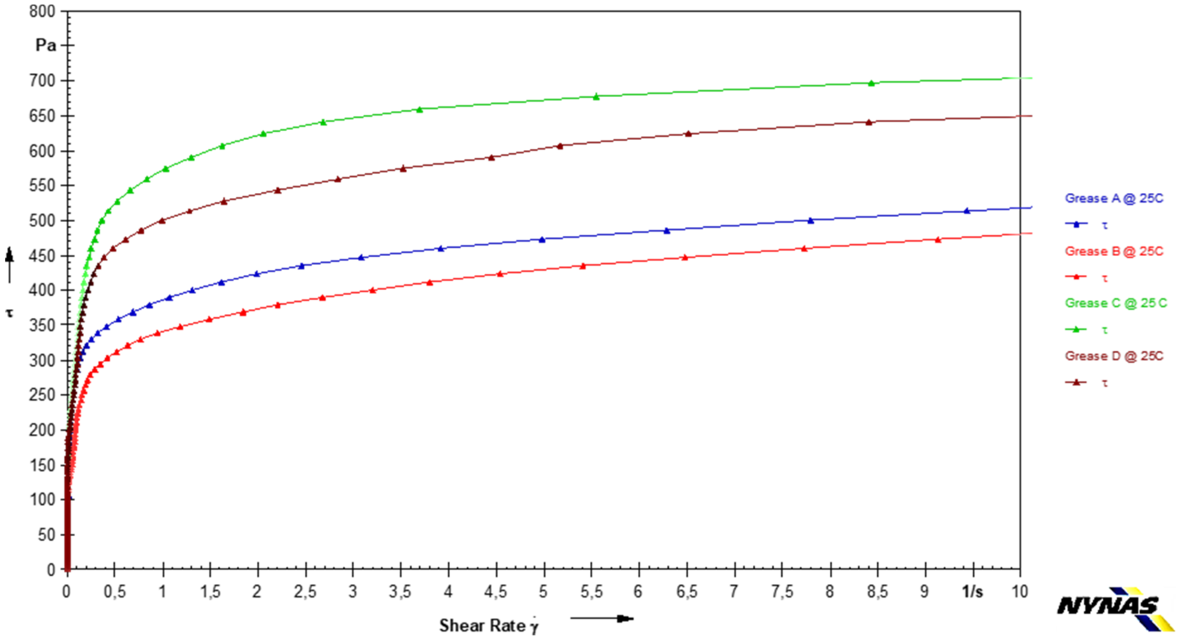

Figure 4. Shear rate as a function of applied Shear stress at constant temperature (25 °C).

Figure 4 suggests that the greases are behaving different when same conditions are applied. For example, the greases show different yield stress despite of the fact that all the greases are classified as NLGI grade 2. Then the question could be: how can we explain the differences? One possible explanation could be found in the unworked penetration numbers for these greases which differ from each other despite of the fact that all are representing NLGI grade 2. The higher the penetration number the lower the yield stress and this is regardless the thickener content.

The dilution effect of incorporating 5 percent "liquid" has also been examined. In summary, it has been found that the use of 5 percent of the ILs dilutes the greases vastly when compared with equivalent amount of an oil (PAO) with almost same viscosity

Figure 5 shows the comparative data for the yield stress drops; 24 up to 43 percent for the ILs, while 11 percent drop for the oil (PAO) could be read off. This finding suggests that the compatibility of the ILs with this type of thickener requires further investigations.

The ratio between the thickener content and the ***ILs***. For instance, if we compare Grease A (lowest thickener content) with Grease D (highest thickener content); the average drop of the yield stress for both ILs is about 41 percent while this is around 26 percent for the Grease D.

Figure 6 demonstrates the dilution effect of the two ILs in comparison with an inert base oil (PAO) with a kinematic viscosity of above 600 mm^2/s (cSt) at 40 °C.

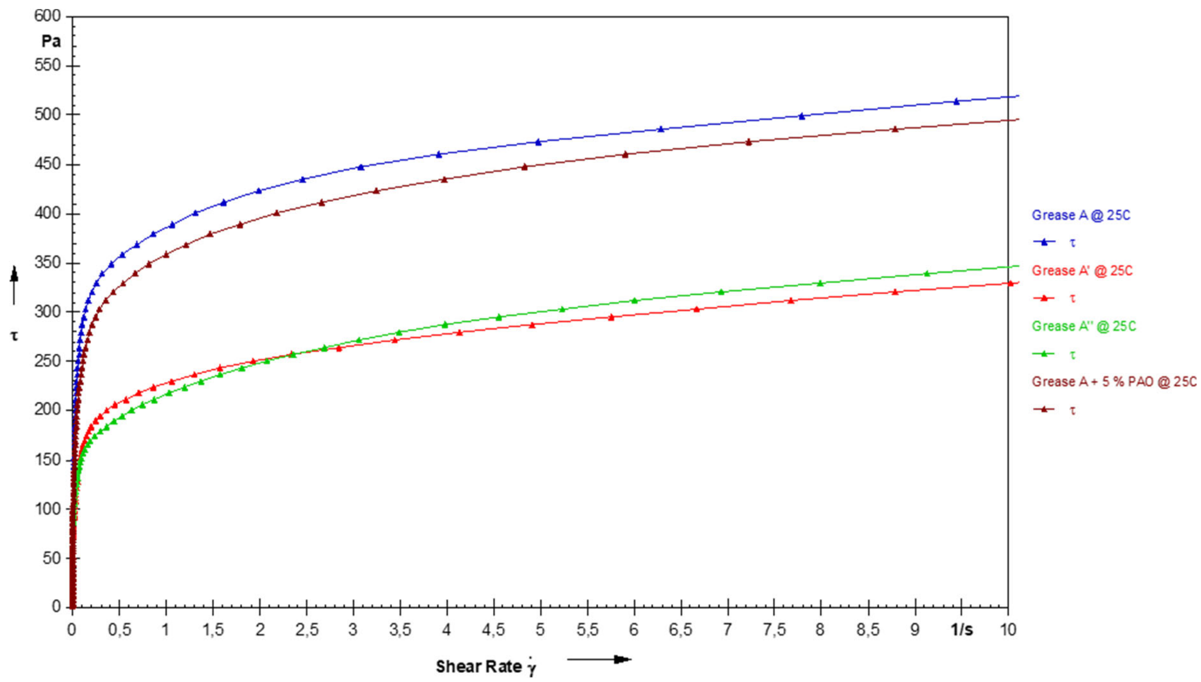

Figure 5 Measure Shear stress vs Shear rate at constant temperature (25 °C).
Grease A' = Grease A + 5 wt% of **IL 4** & Grease A" = Grease A + 5 wt% of **IL 3**

6.2. Copper Corrosion

Copper corrosion is a critical measurement for any lubrication system that will be part of an EV system. Copper is embedded in much of the wiring in EVs and as such compatibility with copper is a critical item to measure. The copper corrosion of the greases before and after the incorporation of the ILs according to ASTM D4048 showed to be excellent, 1a-1b. Figure 6 depicts representative examples of grease B as a neat system as well 5 wt% loadings of ***IL3*** and ***IL4***.

Grease B **Grease B + 5 wt% IL4** **Grease B + 5 wt% IL3**

Figure 6. Copper strips after exposure to neat grease B and formulations with 5 wt% of **IL3** and **IL4** respectively.

6.3. Electrical Conductivity

Higher electrical conductivity is required to prevent arcing in an EV. As such, additives that bring in the right electrical conductivity can have significant performance value to these systems. Lubricants and greases with poor electrical properties may cause electrical discharge damage.[25] Appropriate changes can be made through additives.[26] Lubricants used in EVs endure current flow through the lubricated bearings while protecting the contact surfaces.[27]
The conductivity of greases A and B were measured first in order to get a baseline (Figure7). Conductivity was measured as a function of temperature

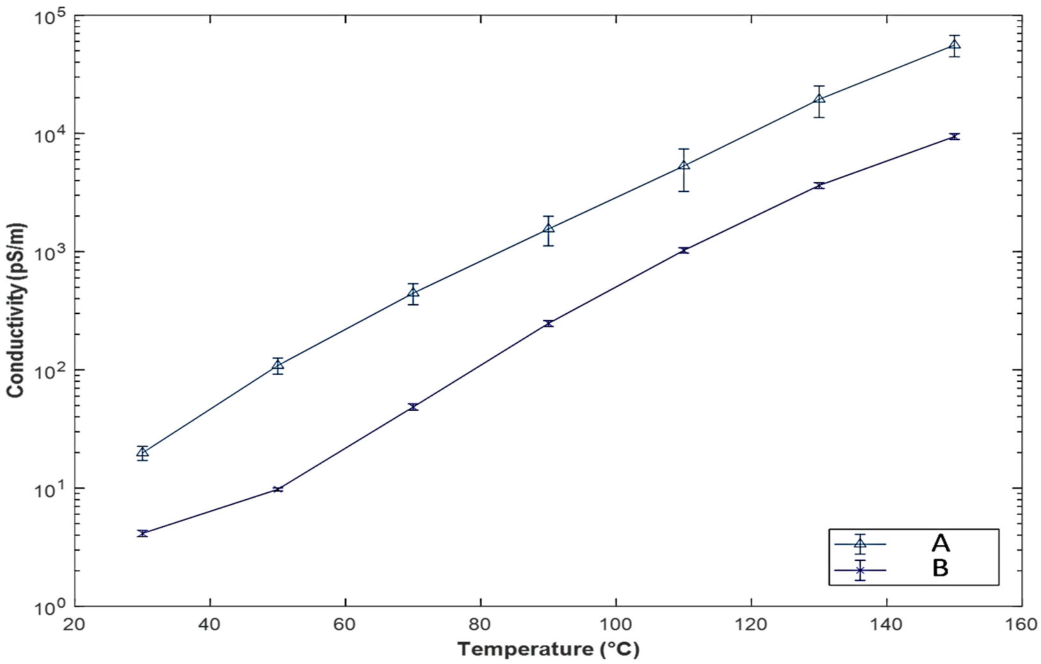

Figure 7: Conductivity of neat greases A and B as a function of temperature

Further to this the conductivity was measured of the mixtures of grease A with 5 wt% of phosphonium salts ***3 (IL3)*** and ***4*** (***IL3***) (Figure 8). A significant increase in conductivity was observed at the 5 wt% loading of both greases. In addition, Grease A which is based on a high naphthenic oil with significantly higher solvency than Base oil A which is used in Grease B.

25. Gunderson, S., Fultz, G., Snyder, C., Wright, J., Gschwender, L., and Heidger, S. (2011). IEEE Trans. Dielectr. Electr. Insul. **2011**, 18, 295
26. Flores-Torres, S., Holt, D. G. L., and Carey, J. T. U.S. Patent 0,100,118A1, April 12, 2018
27. Chen, Y. et al. "Frontiers in Mechanical Engineering", October 2020, 6, Article 571464

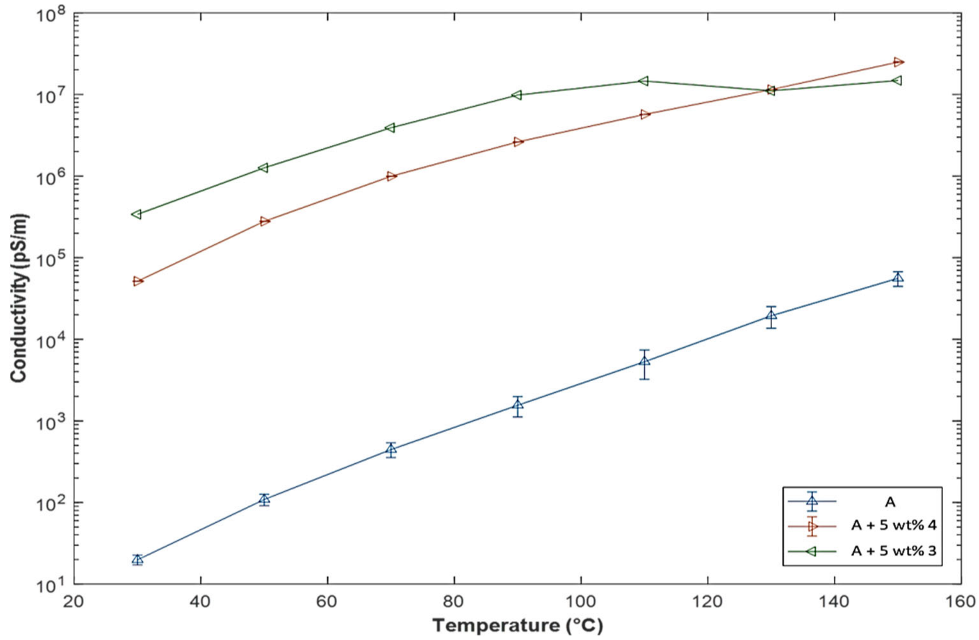

Figure 8: Conductivity vs. time of grease A (blue), grease A + 5 wt% of **IL4** (orange) and 5 wt% of **IL3** (green)

Similarly, the conductivity of grease B was measured as a function of temperature with 5 wt% of phosphonium salts (Figure 9) and similar increases were observed.

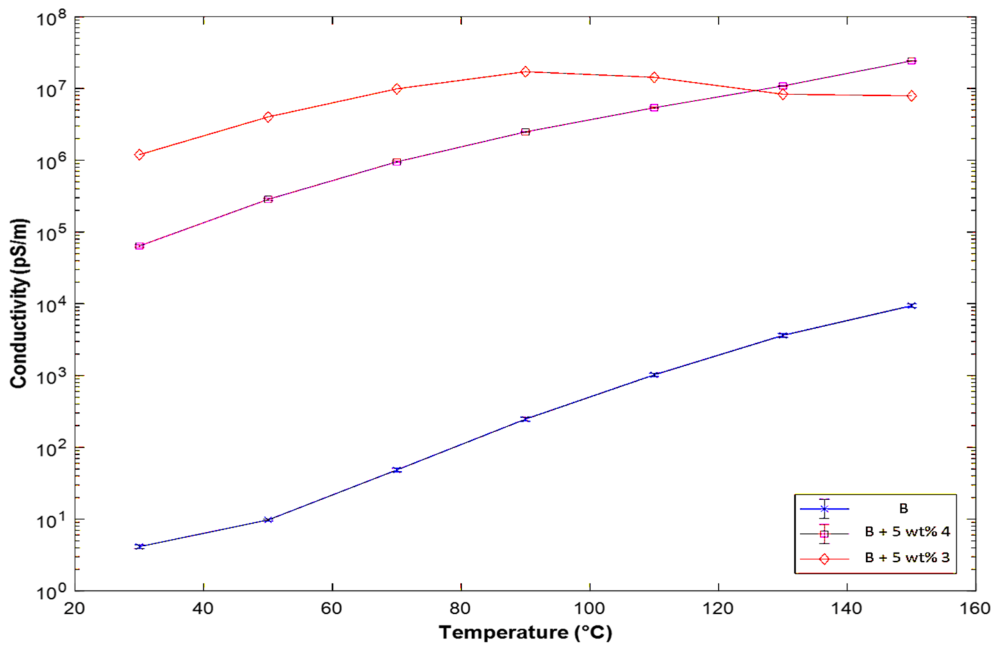

Figure 9: Conductivity vs time of grease B (blue), grease B + 5 wt% of **IL4 (**pink) and 5 wt% of **IL3** (orange)

Of note, in both cases the significant increase in the conductivity validates the potential of the phosphonium salts as additives to increase conductivity in greases. This is in line with other examples in the literature of capabilities of ionic liquids but importantly, validates it within the grease formulations, seeing no negative impact from other additives or components of the grease.

Work remains ongoing to confirm the conductivity of the phosphonium salts in greases C and D. Further to this, we are investigating the effect of lowering and increasing the concentrations of the ionic liquids in these grease formulations to understand the onset of the effect and the highest concentrations to reach the maximum effect.

27.1. Tribological measurements

27.1.1. SRV Tests

The SRV studies were conducted on the grease formulations by using two different methods:

I) **ASTM D5706:** Geometry: ball (Ø = 10 mm) on disk (material 100 Cr 6); Pre-load 50 N for 30 sec, Load 100 N for 15 min; increase 100N every 2 min until Load OK, Stroke 1.5 mm, 50 Hz, 80°C.

II) **ASTM D5707;** Geometry: ball (Ø = 10 mm) on disk (material 100 Cr6); Pre-load 50N for 30 sec; Load 200N for 2 hours; Stroke 1mm; 50 Hz; Temperature: 80°C

The Coefficient of Friction and Wear Volume and Load Ok before the seizure are determined and described in Table 4. Figure 10 shows one of the related graphs.

Table 4. measured Friction of coefficient, the Wear volume and the Load

Remarks	CoF	Wear Volume (mm^3)	Load OK before seizure (N)
Grease B	0.152	0.69	1200 ± 0
Grease B + 1 wt% IL3	0.127	0.50	1100 ± 0
Grease B + 5 wt% IL3	0.092	0	1650 ± 75
Grease B + 1 wt% IL4	0.123	0.23	2000 ± 0
Grease B + 5 wt% IL4	0.152	0	1150 ± 71
Grease C	0.162	0.72	1200 ± 0
Grease C + 1 wt% IL3	0.095	0	1100 ± 0
Grease C + 5 wt% IL3	0.122	0.58	1650 ± 75
Grease C + 1 wt% IL4	0.119	0.54	2000 ± 0
Grease C + 5 wt% IL4	0.152	0	1150 ± 71

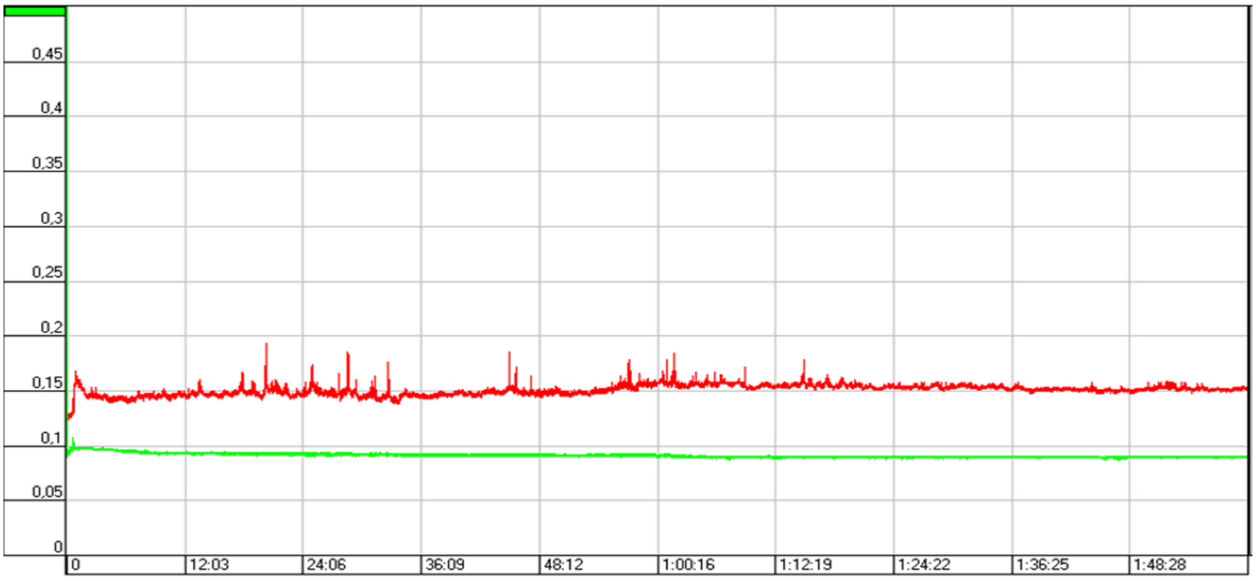

Figure 10: SRV data of Grease B (red) & Grease B with 5 wt% of phosphonium ***IL4***.

Overall, a significant improvement in the COF and the wear was very low throughout the test when the phosphonium IL4 is added to the Grease B at 5 wt% and 1 wt% of IL3 to the Grease C. Ongoing work includes optimizing the wt% of the ionic liquid in this formulation to confirm the minimum loading for effect onset as well as further examinations of the other series of ionic liquids and grease formulations. The initial result is very promising.

27.1.2. Four Ball Tests

In order to determine further the impact of the Ionic liquids on the lubricating greases, four ball tests have been employed, according to ASTM D2266 (40 Kgf / 60 min) and ASTM D2596 (weld load).

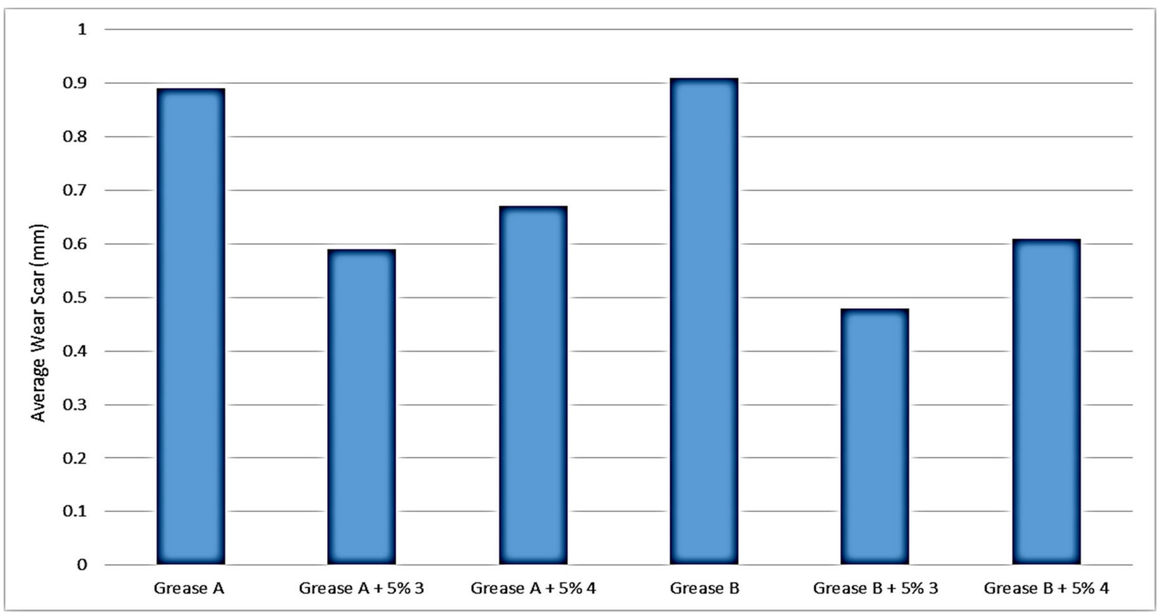

Figure 11. the average wear scar for each sample, according to ASTM D2266.

When reviewing the four ball wear scar averages for the formulated greases versus the greases with ionic liquids there is a noticeable increase in performance on the systems with **IL3** and **IL4** (Figure 11). Of note, Phosphonium **IL3** showed a more significant improvement at the same loading as phosphonium **IL4**.

When evaluating the four ball EP GR Weld test, the systems formulated with 5 wt% ionic liquid systems show improvements to the grease formulations as well with improvements to the seize load. However, in this case phosphonium **IL4** shows higher improvement in grease A while phosphonium **IL3** shows a significantly higher improvement in grease B. The reason for this is currently unclear and remains under investigation.

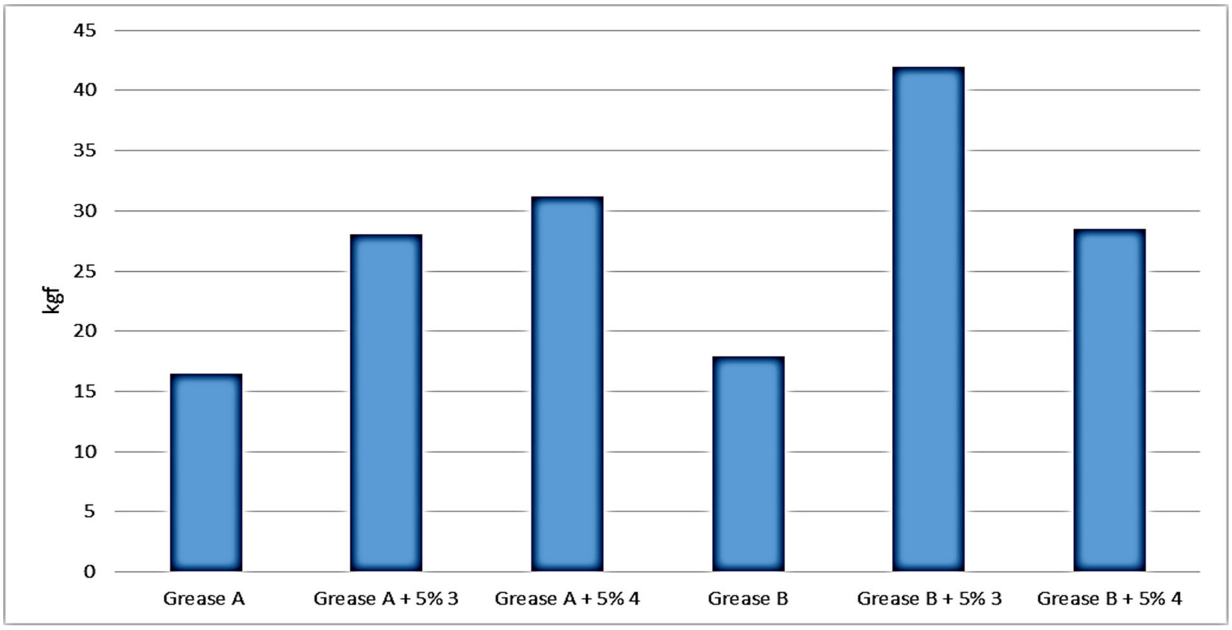

Figure 12. Load-wear Index measurement of greases and formulations by ASTM D2596

The last property measured was the weld point for these six formulations. In this case both ionic liquids showed improvements for grease formulation A (20% improvement), however no measurable differences measured in the formulations of grease B (Figure 13).

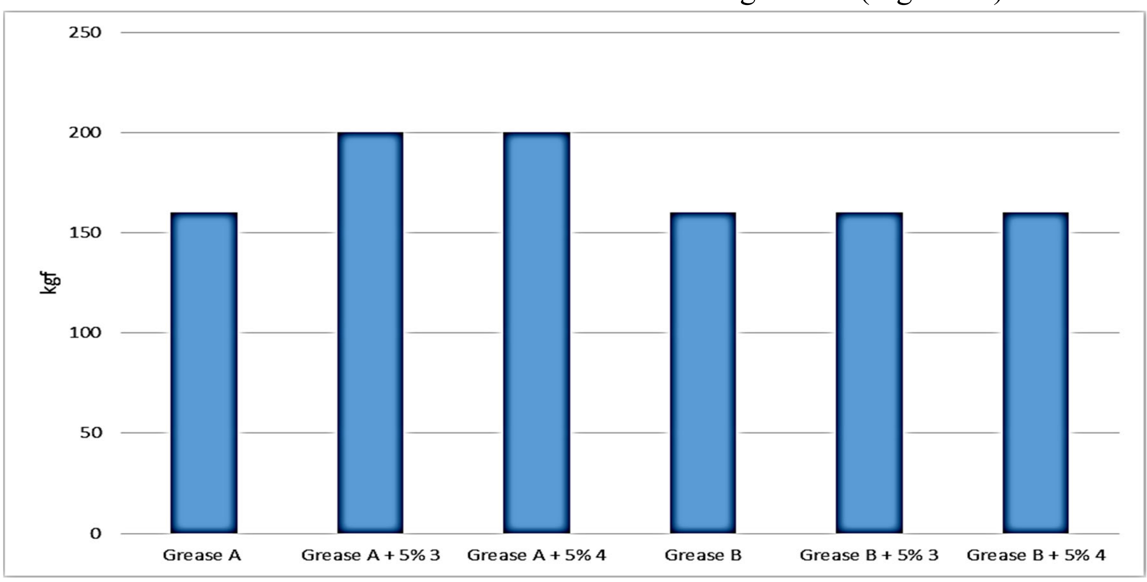

Figure 13 Weld point measurement of greases and formulations by ASTM D2596

Conclusions

Improvements in lubrication continue to be required for electric and internal combustion engine vehicles. Any significant improvement in lubrication for these systems can lead to tangible sustainability improvements, from items such as improved fuel economy or greater efficiency of an electric motor.

Overall phosphonium ionic liquids demonstrate good properties such as high thermal stability, the ability to improve electrical conductivity and proven AW/EP benefits. Furthermore, they meet criteria on EV motors such as being metal free. We have identified 2 candidates for this space and continue to refine formulations to improve the overall efficacy of these systems. We believe that the addition of phosphonium salts, based on these results, to specific greases have potential.

Studies for more advanced testing and more strenuous tests remain ongoing including elastomer compatibility studies.

Appendix – Experimental Procedures and Methods

1. Synthesis of [P4444][DEHP] (3)

12L RBF equipped with: overhead stirrer, addition funnel, H_2O cooled condenser, N_2 supply, thermal well, and hard-shell heating mantle. The reactor was charged with tetrabutylphosphonium chloride in toluene (50.5%, 3015.8 g, 5.16 mol, 1.00 equiv.), 2-ethylhexylphosphate (1666.7 g, 5.16 mol, 1.00 equiv.) and 1796 g of water. A solution of NaOH (50%, 476.3 g, 5.94 mol, 1.15 equiv.) was added drop wise at 60oC over 1.25 hrs. After the addition was completed, the mixture was left to digest at temperature overnight. The following day the aqueous layer was drained (1680 g). Following this, the product was washed three times with RO water. After the third wash, an emulsion formed resulting in poor separation between aqueous and organic layers. An additional 1704 g of water was added; however, this did not improve separation. The mixture was left undisturbed for 5 days, at which point there was separation between the layers along with a rag layer. The %Cl was measured through $AgNO_3$ titration after the last wash. The results were low enough (%Cl=0.02) to proceed to the strip without further washes.

This is an adapted synthesis of a literature method[28]

2. Synthesis of [P8888][DEHP] (4)

12L RBF equipped with: overhead stirrer, addition funnel, H_2O cooled condenser, N_2 supply, thermal well, and hard-shell heating mantle. The reactor was charged with tetraoctylphosphonium bromide (52.9%, 3970 g, 3.73 mol, 1.00 equiv.), 2-ethylhexylphosphate (1201 g, 3.73 mol, 1.00 equiv.) and 2000 g of water. A solution of NaOH (50%, 312 g, 3.91 mol, 1.05 equiv.) was added drop wise at 50^{o}C over 1.75 hrs. After the addition was completed, the mixture was left to digest at temperature overnight. The following day the aqueous layer was drained (1824 g). Following this, the product was washed five times with RO water. After the last two washes, the organic and aqueous layers were titrated with $AgNO_3$ to determine %Br.

3. Synthesis of tributyl(methyl)phosphonium tosylate (6)
Synthesized as per reference[24]

4. Synthesis of tributyl(ethyl)phosphonium diethyl phosphate (7)
Synthesized as per reference[24]
Formulation of Greases
Incorporation of the Ionic Liquids into the greases were conducted in two steps. Step 1: hand mixing with spatula for one minute. Step 2: four time run through the three-steel-roller mill with minimum gap size

5. TGA Method Description

28. Barnhill, W. C. Qu, J. et al. Applied Materials & Interfaces, **2014**, 6, 22585
TGA were run on a TGA Q50 V20.10 Build 36 by ramp method (10 C/minute ramp) under air and/or nitrogen. These were run from room temperature to 500 Celsius.

6. SRV Methods Description

ASTM D5707 - standard test method for measuring friction and wear properties of lubricating greases using a high frequency, linear oscillating (SRV) test machine. Geometry: ball (Ø = 10 mm) on disk (material 100 Cr6); Pre-load 50N for 30 sec; Load 200N for 2 hours; Stroke 1mm; 50 Hz; Temperature: 80°C

ASTM D5706 – Standard test method for determination of load carrying capability of lubricating grease, even called step load test. The conditions used in this study are; Geometry: ball (Ø = 10 mm) on disk (material 100 Cr 6); Pre-load 50 N for 30 sec, Load 100 N for 15 min; increase 100N every 2 min until Load OK, Stroke 1.5 mm, 50 Hz, 80°C

7. Electrical Conductivity Method Description
Electrical conductivity was measured with an Epsilon system for the measurement of dielectric fluid properties. A ramp of temperature from 30°C to 150°C was tested, for a range of conductivity between 0.02nS/m to 600nS/m. Ten points are acquired through slow heating rate (repeatability done on 2 tests with 8g of grease). Samples don't need pretreatment and the cell need to be properly cleaned with isopropanol several times between each sample.

8. Viscosity Measurements
SVM 3000, Stabinger Viscometer from Anton Paar was used for viscosity measurements. Dynamic viscosity and density were measured at a given temperature and from those values kinematic viscosity was internally calculated by the SVM 3000 software. All measurements were done in a slow with repeat mode (F6), at 20 °C, 25 °C and 40 °C.

9. Four ball AW test and Four Ball EP GR Weld Test
Four ball wear tests were performed in accordance to ASTM D2266-B method. Test was performed at a load of 40 kgs, 1200 rpm, 75 Celsius. Four ball EP GR Weld test was performed according to ASTM D2596.

Investigation Of The Possibility Of Obtaining Greases Based On Calcium Sulfonates With Different Tbn

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Abstract

The uniqueness of the properties inherent exclusively in greases allows the use of these products in various friction units. At the same time, the range of greases produced should include products that are workable in conditions of low and high temperatures, heavy loads, as well as in humid and aggressive environments. One of the products from among the greases that meet such requirements are greases thickened with calcium sulfonates.

Calcium sulfonates, differing in the value of the alkaline number (from neutral products up to 500 TBN), are primarily used as detergent-dispersing additives for motor oils. However, studies conducted by the authors show that calcium sulfonates with 140 TBN or more can be successfully used as thickeners of greases.

As part of the work, samples of greases thickened with calcium sulfonates with 140, 300, 350 and 400 TBN were obtained. The results show that the strength of the formed framework of the grease depends on the value of TBN of the calcium sulfonate used. Since the content of the active substance (calcium sulfonate) in the analyzed products is the same, the authors associate the results obtained with a higher content of calcium hydroxide and calcium carbonate in highly alkaline products, which, as a result of transformations, form stronger calcite micelles, which are the centers of the sulfonate grease framework.

In general, the conducted studies allow us to conclude that in order to obtain sulfonate greases that work in a wide range of loads and temperatures, showing stability of properties regardless of operating conditions, it is necessary to use synthetic calcium sulfonates as a thickener, not petroleum ones. In this case, the resulting products can also be used as food greases.

Introduction

Calcium sulfonate greases are one of the promising types of high- temperature greases, which may well become "universal" due to a number of their natural properties:

- high dropping point (above 300°C);
- excellent protective properties;
- high performance in the presence of water, as well as under the action of acidic or alkaline media;
- excellent mechanical stability;
- high extreme pressure characteristics;
- possibility of application in low temperature conditions.

The fields of application of calcium sulfonate greases are diverse, today they are successfully used in bearings of machines and equipment operated under high loads and temperatures, in the presence of water and mechanical contamination, that is, in the automotive, steel, construction, mining, marine, food industry, as well as at nuclear power plants [1].

Calcium sulfonate cannot be called an absolutely new type of thickener, the idea of using it as a thickener for greases was formed and was first implemented more than half a century ago, when it was found that in a sufficiently high concentration it provides the necessary thickening effect [2,3].

Calcium sulfonate greases are made by converting a liquid detergent that contains amorphous calcium carbonate into a lubricant containing calcite particles. Due to its own lubricating properties of calcite particles, conventional anti-wear additives become unnecessary. It is precisely because of the absence of these additives that some calcium sulfonate greases are attractive for the food industry.

It is known that by origin calcium sulfonates are divided into petroleum and synthetic. Petroleum sulfonates are obtained mainly by direct sulfonation of petroleum products (distillate and residual oils) with subsequent purification and neutralization of the resulting mixture of sulfonic acids. This causes, first of all, the heterogeneity of their hydrocarbon composition. Synthetic calcium sulfonates are produced from high-boiling alkylbenzenes, which makes it possible to obtain a product with a relatively homogeneous hydrocarbon composition [4,5].

Depending on the metal content, neutral, medium- and high-alkaline sulfonate additives are distinguished. Neutral products cannot be used as thickeners of greases, since their composition lacks the main component - calcium carbonate.

However, the higher the total base number (TBN) of the additive, the higher the thickening capacity of calcium sulfonate, as shown by the results of this study.

Experimental Details

The study analyzed four types of calcium sulfonate, which are produced by LLC "NPP Qualitet". Their physico-chemical properties are shown in Table 1.

Table 1. Physico-chemical properties of used calcium sulfonates

Property	K-311	K-312	K-313	K-314
Kinematic viscosity at 100°C, cSt	<100	<100	<150	<60
Total Base Number, mg KOH/g	140	300	400	350
Calcium Sulfonate, %	28,0	28,0	24,0	24,0
Calcium, %	5,6	11,7	15,6	13,8

Based on them, samples of sulfonate lubricants were prepared in the usual way. Additional components (structure-forming agents) were kept the same.

Base oils (petroleum and synthetic) of various viscosities were used as dispersion media.

For all the samples obtained, worked penetration, dropping point, tribological properties and water washout resistance were determined and the obtained values were compared with each other.

Results and Discussion

The results of the study of the operational properties of base greases prepared on the base oil of group 2 are presented in Table 2 (the base oil viscosity of all grease types was kept in ISO VG 180). All lubricants have a high level of operational properties, including satisfactory anti-wear and extreme pressure (EP) properties. Water washout resistance increases with an increase in the TBN of calcium sulfonate used. It is also noted that with a constant ratio of components, the use of calcium sulfonate with an alkaline number of 150 as a thickener makes it possible to obtain a lubricant with consistency in NLGI 2 at 291, while samples obtained on the basis of calcium sulfonate with an alkaline number of 300-400 have consistency in NLGI 3 at 241-260.

When using a low-viscosity base oil, the water washout resistance of a sample prepared using calcium sulfonate with an alkaline number of 150 sharply deteriorates. The results are provided in Table 3. However, all the samples obtained are with consistency in NLGI 2. There is an improvement in the tribological properties of grease samples when using PAO-4 synthetic oil. The results are provided in Table 4. The anti-wear effect of greases is provided mainly due to the formation of a boundary lubricating film on the metal surface. The improvement of the anti-wear properties of greases when using synthetic oil is explained by the absence of surfactants in such oil that prevent the formation of a protective film of calcium sulfonate.

Table 2. Test results of operational properties of base greases (ISO VG 180)

Property	K-311	K-312	K-314	K-313
Penetration, worked 60x, dmm	291	260	253	241
Dropping point, °C	>250	>250	>250	>250
4 Balls Wear (40 kg, 1hr), mm	0,63	0,52	0,50	0,50
Four-Ball Weld, kgf	400	562	630	>630
Water Washout, 79°C, % loss	5,28	3,21	3,14	3,06

Table 3. Test results of operational properties of base greases (low-viscosity base oil)

Property	K-311	K-312	K-314	K-313
Penetration, worked 60x, dmm	303	287	283	279
Dropping point, °C	235	>250	>250	>250
4 Balls Wear (40 kg, 1hr), mm	0,59	0,50	0,49	0,47
Four-Ball Weld, kgf	422	562	>630	>630
Water Washout, 79°C, % loss	7,72	3,44	3,32	3,28

Table 4. Test results of operational properties of base greases (PAO-4)

Property	K-311	K-312	K-314	K-313
Penetration, worked 60x, dmm	301	288	283	280
Dropping point, °C	>250	>250	>250	>250
4 Balls Wear (40 kg, 1hr), mm	0,52	0,46	0,43	0,42
Four-Ball Weld, kgf	596	630	>630	>630
Water Washout, 79 °C, % loss	7,59	3,26	3,19	3,07

The final stage of the study is the comparison of greases thickened with calcium sulfonates of petroleum and synthetic origin.

The first sulfonate additives were obtained from petroleum raw materials, and the product was obtained with a low alkaline number, which caused its low neutralizing and dispersing properties. In addition, despite the selection of fractional composition and special purification, the structural and group composition of raw material is characterized by a wide range of different hydrocarbons. Some of these hydrocarbons are suitable for the production of sulfonate additives, others, in turn, form a mass of by-products that require mandatory removal from the mixture. Alkylbenzenes suitable for the production of petroleum calcium sulfonates are contained in specially prepared raw materials in limited quantities and have a wide spread in molecular weight and, therefore, have side radicals of different lengths, both optimal, having in their chain from 16 to 26 carbon atoms, and with shorter, as well as longer chains. Thus, the presence of undesirable components negatively affects the production technology and, accordingly, the quality of commercial calcium sulfonates.

At the same time, various sulfonic acids are used as raw materials for the production of synthetic calcium sulfonates, both with single linear radicals with a side chain length of 16-26 carbon atoms, and with two side chains of 10-14 carbon atoms each. Calcium sulfonates obtained on the basis of such raw materials have higher performance characteristics and, as a rule, such additives are used in the production of additive packages for modern oils.

Greases were prepared in the usual way, using petroleum and synthetic calcium sulfonates with TBN of 300 as a thickener. Synthetic PAO-4 oil was used as a dispersion medium. The results are provided in Table 5.

Table 5. Test results of operational properties of base greases on oil and synthetic calcium sulfonates

Property	Oil calcium sulfonate	Synthetic calcium sulfonate
Penetration, worked 60x, dmm	247	288
Dropping point, ^oC	>250	>250
4 Balls Wear (40 kg, 1hr), mm	0,57	0,46
Four-Ball Weld, kgf	630	630
Water Washout, 79^oC, % loss	4,17	3,26

As can be seen from Table 5, petroleum calcium sulfonate affects the penetration of the grease (sample with penetration in NLGI 3 at 247). Since NLGI 2 products are the most convenient for use in centralized lubrication systems, the results obtained can be considered unsatisfactory. There is also a negative effect of petroleum calcium sulfonate on anti-wear properties and resistance to water washout. Based on the results obtained, it can be concluded that the use of synthetic calcium sulfonates as thickeners of greases is more preferable.

Conclusions

The tightening of the modes of operation of friction units in modern mechanisms inevitably leads to the search for lubricants that work in a wide temperature range and, at the same time, maintain a high level of operational characteristics for a long time. One of such materials are sulfonate greases, which, due to their excellent natural characteristics, are gaining more and more popularity as "universal" greases.

The results of the study show that in order to obtain high-quality greases capable of operating in a wide temperature range, under high loads and in the presence of water, careful selection of grease components is necessary. Thus, it is preferable to use calcium sulfonate with TBN of 300 or more, since the value of TBN has a direct effect on the strength of the lubricant frame, on the level of tribological properties and water washability. In addition to TBN, it is important to pay attention to the origin of calcium sulfonates, since, as the results of the study showed, synthetic products are more preferable for obtaining high-quality products. At the same time, the selection of base oil is also important. The study shows that the use of synthetic oils (namely PAO) leads to an improvement in anti- wear properties without the addition of appropriate additives. This fact, as mentioned earlier, is a huge advantage, since such greases can be used in the food industry.

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